Indian J. Phys. 77A (2), 99–102 (2003)

AN INTERNATIONAL JOURNAL IJPA

Some recent aspects of IV–VI based diluted magnetic semiconductors

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Abstract . This invited talk begins with a brief review of the progress made in semiconductor physics and devices in the last century. A concise historical sketch of research in IV–VI semiconductors is also presented. Some novel features of diluted magnetic semiconductors (dms) based on IV–VI systems are highlighted. Finally, recent results obtained by the authors's group are discussed.

Keywords : Diluted magnetic semiconductors, IV–VI semiconductors, magnetic transition and magnetisation.

PACS Nos. : 71.20.Nr, 75.50.Pp

1. Introduction

Semiconductors and magnetism separately constitute two important branches of condensed matter and materials physics. Both the subjects are rich in physics and have also contributed to high technology. Diluted magnetic semiconductors (dms) are materials where a small percentage of non-magnetic cations in the host material is replaced by the magnetic ions. The magnetic properties of these materials are controlled by both localised magnetic moments and free carriers. The exchange interaction between both types of electrons also plays a significant role. The DMS based on IV–VI semiconductors show, among other properties, high field magnetisation, carrier concentration–dependent ferromagnetic transition and photo induced magnetisation.

The planning of the article is as follows : In Section 2, a brief history of the development of semiconductor physics in general and IV–VI semiconductors in particular is presented. Section 3 contains a brief review of some novel characteristics of the IV–VI based dms, including a brief review of recently obtained results by our group. Section 4 summarises the article and presents the concluding remarks.

2. Brief history of semiconductor physics

2.1. *Milestones :*

In 1931, Wolfgang Pauli commented : "One should not work on semiconductors, that is a filthy mess, who knows whether they really exist" [1]. Since then the physics and also the technology of semiconductors has developed in a big way. According to Hoddeson *et al* [2], a semiconductor was first identified as a distinct class of materials by Edward Grunejsen by 1922. The advent of quantum mechanics in the first quarter of the last century led to a better understanding of metals and insulators. On the other hand, A H Wilson [3,4], in a series of papers and books, applied quantum theory to semiconductors to distinguish its nature from that in metals and insulators. The first book which was entirely devoted to semiconductors was written by A F Ioffe [5]. Semiconductors became important when, after the second world war, Bardeen, Brattain and Schockley reported the discovery of transistor action [6]. In 1950 Schockley wrote an excellent book in semiconductor physics [7]. The development of the effective mass theory by Luttinger and Kohn [8] laid the foundation of understanding impurity states in semiconductors. While on the physics side the contributions of P W Anderson and N F Mott [9] enriched the subject. Esaki [10] made valuable contributions to semiconductor devices. With the discovery of quantum Hall effect [11], semiconductor physics became a fashionable and high-theory-content physics.

At this juncture, it would be worthwhile to mention about early Indian contributions to the physics of semiconductors by Sir J C Bose [12]. In 1954, Pearson and Brattain [13] gave priority to Bose for the use of a semiconducting crystal as a detector of radio waves. Nevil F Mott credited Bose as "being at least sixty years ahead of his time", adding further that "Bose anticipated the existance of p- and n-type semiconductors" [14].

2.2. *Early developments in IV–VI semiconductors :*

The IV–VI semiconductors which include lead chalcogenides, SnTe and GeTe are narrow gap semiconductors with carrier densities varying from 10^{18}–10^{21} cm^{-3}. Much before the understanding of semiconductor physics, lead sulfide was used as a detector in crystal radio receivers [15]. During the second world war PbS was used as an infrared detector [16]. Russians used lead chalcogenides as thermoelectric generators [17]. On the physics side, there was a controversy in early fifties on the magnitudes of the energy gaps in lead salts. However the controversy was resolved in favour of narrow energy gaps (~0.2 eV). The first band structure calculation for a semiconductor was done for PbS [18]. Superconductivity was discovered in GeTe and SnTe, with very low transition temperatures [19]. Excellent reviews on lead salts are found in the works of Dalven [20] and Nimitz [21].

3. Novel features of IV–VI based dms

The VI–VI based dms are a class of novel materials which show very interesting and unique properties. The magnetic properties of these materials are determined by antiferromagnetic interactions which are weaker than those of narrow gap II–VI compounds [22,23]. The Eu–Eu exchange effects are even weaker in comparison to those of Mn–Mn, as expected [24].

3.1. *Carrier induced magnetic phase transition :*

The magnetic phase transition of Pb (0.28) Mn (0.72) Te show a rich variety of magnetic phases induced by carrier concentrations [25]. At a carrier (hole) concentration of $p_c = 3 \times 10^{20}$ cm^{-3}, an abrupt change in the magnetic phase, measured at temperature ($T > 1, 5$ K), from a paramagnetic to a ferromagnetic state takes place. This transition, which was first found by Story *et al* [26] is imposed by the band structure of the materials [27]. If the concentration of the carriers is increased further, the oscillations in the RKKY interaction become important. At higher carrier concentrations ($p > p_c$), this period is shorter and antiferromagnetic interactions start to compete with ferromagnetic interactions, inducing a spin glass state. This transition to the spin glass state is a gradual transition and an intermediate phase, the reentrant spin glass phase, is also observed [28].

3.2. *Layered IV-VI dms :*

The study of magnetic properties in quasi two dimensional systems is of particular interest for some novel aspects of magnetism and of fundamental importance for an understanding of the electronic properties in these systems The first experiment of this kind was a susceptibility study on PbTe/EuTe short period superlattices [29]. PbTe is diamagnetic [30,31]. EuTe is paramagnetic and below 9.58 K, antiferromagnetic. Susceptibility measurements of $(EuTe)_m/(PbTe)_n$ layer structures with (m, n); (1, 3); (2, 6) and (4, 4), and periods between 100 and 400 reveal the following features. For the (4, 4) sample the antiferromagnetic phase transition is indeed observed at the Neel temperature of $T = 8.5$ K, only slightly below the bulk value for EuTe. No phase transition was observed for the (2/6) and (1/6) samples where the Eu atoms do not have all their six nearest neighbours in contrast to the (4/4) sample [32].

3.3. *Light induced magnetisation :*

Light induced magnetisation is a method by which spin polarised carriers are created through interband excitation using circularly polarised light [33]. The spin polarised carriers interact *via* the exchange interaction with the Mn-ions in $Pb_{1-x}Mn_xTe$ and induce a magnetic moment which is detected by sensitive squid methods. This method was extended [34] to a study of $Pb_{1-x}Mn_xTe$/PbTe quantum structures when a periodic sequence of diamagnetic wells (PbTe) is embedded in sequence of paramagnetic $Pb_{1-x}Mn_xTe$ barriers. If the excitation energy of the layer is lower than the band gap of $Pb_{1-x}Mn_xTe$ which forms the barrier, spin polarised carriers are created within the PbTe wells only. However, due to the leakage of the wave function of the carriers confined within the diamagnetic wells into the paramagnetic barriers, the Mn ions can be polarised as a consequence of the contact spin-spin exchange interaction.

3.4. *Other electronic and magnetic properties :*

There have been some measurements of the high field magnetisation in IV–VI semiconductors with Mn, Eu, Gd, Fe ions [35–39]. We have done calculations to explain some of these observations in Pb(Mn,Eu)Te [30,40]. It is found that in both the cases, the single spin contributions are dominant. However, at high concentrations of magnetic ions, contributions from two and three spin clusters become appreciable. The results sometimes depend on assumptions, whether or not are the spins random. The results are also sensitive to anti-ferromagnetic interactions leading to frozen spins. The diamagnetic contributions are also taken into account. Since experiments are performed for materials with carrier densities of about 10^{18} cm^{-3}, the spin polarisation contributions from carriers are found to be insignificant. Calculations for the effective masses and g-factors reveal interesting anisotropic effects in the electronic structure, arising from the spin-orbit and sp–d/f hybridisations [40].

3.5. *DMS as half metallic magnets :*

Before conclusion, I would like to give an account of recent developments in a kind of materials known as half-metallic magnets (HMM) [41]. It is believed that some dms, such as GaMnAs, HgMnSe could be good candidates for this kind of materials. In HMM one kind of spin band is partially full, showing metallic character and the other kind is either empty (above the Fermi level) or full (below the Fermi level) showing insulating behaviour. In other words, these materials show spin-polarised current. These materials could be possible candidates for spintronics.

4. Conclusion

In this this article, starting from a brief history of the developments in semiconductors, I present some recent aspects of IV–VI based dms, justifying their categorisation as novel materials. The unique and interesting features of these dms underscore not only their importance in the cutting edges of condensed matter physics but also in devices and materials.

Acknowledgment

The research was supported by the University Grants Commission (UGC), New Delhi.

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